

# Separation of the strain and finite size effect on the ferromagnetic properties of $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ thin films

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The ferromagnetic properties of epitaxial  $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$  thin films have been studied. The magnetic transition is affected by both strain and finite thickness. We have used a series of films of different thickness and on different substrates in order to quantitatively determine the change in Curie temperature contributed by each effect. The phase diagram of  $T_C$  versus in-plane strain suggests that the ferromagnetic transition temperature is suppressed by tensile strain and enhanced by compressive strain. The general method of separating strain and finite thickness effects should be applicable to any ordering phase transition in thin films.

Thin films of perovskite oxide materials have attracted great attention lately due to their potential technological applications based on a variety of appealing physical properties, such as colossal magnetoresistivity, ferroelectricity, and high- $T_C$  superconductivity. The properties of films differ from the corresponding bulk typically due to a combination of three factors. Firstly, defect levels are often higher in films. Oxygen deficiency is the most common defect and will typically suppress the transition temperature due to the decrease of doped hole density or the destruction of metal-oxygen hopping pathways.[1] Secondly, finite size effects may be important. For example, the Curie temperature ( $T_C$ ) for a ferromagnetic thin film will be reduced when the spin-spin correlation length exceeds the film thickness. The thickness-dependent Curie temperature has been most carefully studied in simple metallic films of Fe, Co, Ni and Gd. [2, 3] A similar scaling effect has also been found in ferroelectric materials.[4] Thirdly, strain incorporated into films due to effects such as a lattice mismatch with the substrate may also alter the phase transition through changes in fundamental interactions that depend upon atomic spacing. Strain in thin films is often thought of as analogous to that induced in high-pressure experiments on bulk materials. However, a much larger strain can be achieved in films than that in bulk and the strain in films is usually biaxial rather than hydrostatic or uniaxial as in most bulk pressure experiments. The induced strain can modify the lattice structure, the critical temperature for phase transition, and sometimes the nature of the phases present themselves. [5, 6, 7]

$\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$  (LSCO) is a highly doped ferromagnetic oxide material with perovskite structure and has desirable properties of high electrical conductivity and large magnetoresistance. [8, 9] Thin film LSCO is a candidate for applications such as electrodes for fuel cells, ferroelectric memory and spin valve devices. The first concern noted above, the oxygen content in LSCO films, can be controlled by carefully optimizing growth conditions so that stoichiometry of oxygen can be maintained. [10]

However, the finite size and strain effects are intrinsic to the film, and it is not trivial to separate the influence of these two effects on a particular film. Recently, Fuchs et al [11] and Andres et al [12] have reported the finite thickness effect for the perovskite oxide films,  $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$  and  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ , respectively. However, the possible effects of strain were discounted in the analysis. Conversely, studies concerned with the effect of strain have neglected finite size scaling. [13] Clearly it is necessary to consider both possible effects on an equal footing and it would be desirable to assign a particular amount of change in transition temperature to a particular cause. In this paper, we report a systematic study of the Curie temperature of a series of ferromagnetic LSCO films with different thickness on a variety of substrates. This allows us to separate the finite thickness effect from the direct effect of strain and thus construct a  $T_C$  versus strain phase diagram.

LSCO films were epitaxially grown by a pulsed laser deposition technique from a stoichiometric target. Deposition was carried out using a 248 nm KrF excimer laser at 2 Hz, with a substrate temperature of 750 °C, in an atmosphere of 200 mTorr  $\text{O}_2$ . After growth the films were slowly cooled in 300 Torr  $\text{O}_2$ . The fact that our thickest films with little strain had a  $T_C$  very close to the bulk value ( $\approx 250$  K) is an indication that this procedure produces film with near stoichiometric oxygen. A set of films with thickness varying from 11 nm to 126 nm were grown on  $\text{LaAlO}_3$  (LAO) and  $\text{SrTiO}_3$  (STO). For a thickness of 22 nm, LSCO films were also grown on  $(\text{LaAlO}_3)_{0.3}(\text{Sr}_2\text{LaTaO}_6)_7$  (LSAT) and  $\text{SrLaAlO}_4$  (SLAO) substrates.

Structural characterization of the films was carried out using a conventional powder x-ray diffractometer and a four circle diffractometer with a general area detector Diffraction System (GADDS) at room temperature. The only peaks observed in the normal  $\theta$ - $2\theta$  scans are from the (00 $l$ ) type peaks indicating the absence of impurity phase or grains with other orientations. The in-plane and out-of-plane lattice parameters were determined by

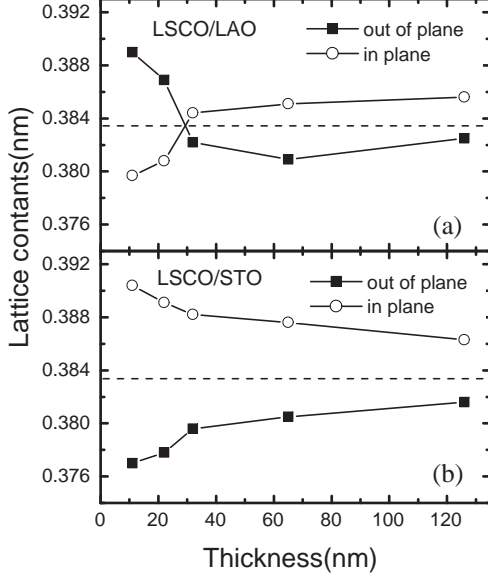


FIG. 1: Film thickness dependence of the measured in-plane (circles) and out-of-plane (squares) lattice parameters of epitaxial LSCO films grown on (a) (001) LAO and (b) (001) STO substrates. The bulk parameters of the LSCO target are indicated by the horizontal dashed line. The size of the error bars is smaller than that of the symbols.

normal and off-axis diffraction. The field-cooled DC magnetic properties were measured using a superconducting quantum interference device (SQUID) magnetometer in a range of 5 K to 320 K at a magnetic field of 100 G with the applied field direction parallel to the sample surface. Since the transitions were slightly rounded, we determined  $T_C$  by extrapolating the linear portion of the magnetization curve just below the transition.  $T_C$  is defined as the point where this line intercepts the paramagnetic background.

The in-plane and out-of-plane lattice parameters for films of LSCO with various thickness on LAO and STO substrates are shown in Fig. 1. These lattice constants determine the strain state of the films. Bulk LSCO is a distorted perovskite with a cubic lattice parameter of 0.3834 nm, shown as a dashed line in the figure. On both substrates, the thinnest films appear to be coherent in plane with the substrates. The thinnest film on STO is under a large tensile strain and undergoes a monotonic relaxation as the film thickness increases. The films on LAO show somewhat different behavior. The thinner films are under compressive strain, but thicker films show a small tensile strain similar to the thicker films on STO. This appears to indicate that the misfit strain at higher temperature is completely relaxed in these thicker films and the remaining strain results from the difference in the thermal expansion coefficients between the films and the substrates.[14, 15]

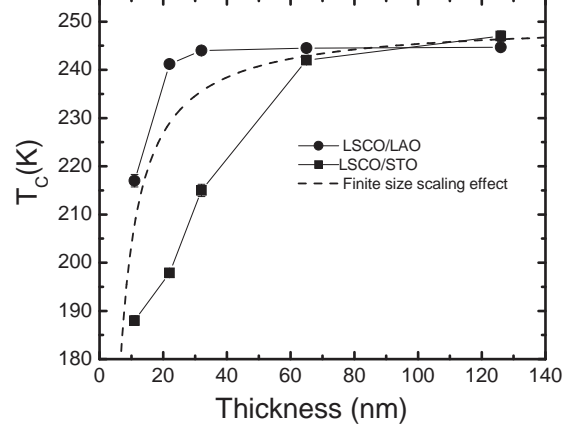


FIG. 2: Film thickness dependence of  $T_C$  for epitaxial LSCO thin films grown on LAO and STO. The dashed line is our calculation for  $T_C$  based on finite size scaling alone as described in the text.

Fig. 2 shows the Curie transition temperature vs film thickness for LSCO on LAO and STO, respectively. On both substrates,  $T_C$  is substantially reduced for the thinnest films, gradually increases with increasing thickness, and eventually reaches a value near that of the bulk. However, the thin films on LAO show a significantly higher Curie temperature than those on STO, most markedly in the thinner regions. As seen from Fig. 1, below 30 nm, the films on STO are under tensile strain while those on LAO are compressed. Since the finite size effect ought to be independent of choice of substrate, it appears that the phase transition temperature is sensitive to the strain induced by the substrates as well as finite size.

It is well known that the finite size effect will suppress the Curie temperature when the film thickness is below a certain critical value. According to critical behavior scaling theory for a magnetic phase transition, [3]

$$[T_c(\infty) - T_c(d)]/T_c(\infty) = (c/d)^\lambda \quad (1)$$

where  $T_c(\infty)$  is the ferromagnetic Curie temperature in the bulk limit,  $d$  is the film thickness,  $\lambda$  is the critical shift exponent whose value reflects the universality class of the phase transition, and  $c$  is a constant related to the spin-spin correlation length. To produce a sample that is only affected by the finite size effect one would need a substrate with the same lattice constants and same thermal expansion as the LSCO films, which is not possible. We have followed a converse strategy. Thin films with the same thickness are grown on a variety of substrates with different lattice constants, so that each film will have the same finite size scaling effect but different strain. We have chosen to focus on films of thickness 22 nm on four different substrates. These are LAO(0.3790 nm),

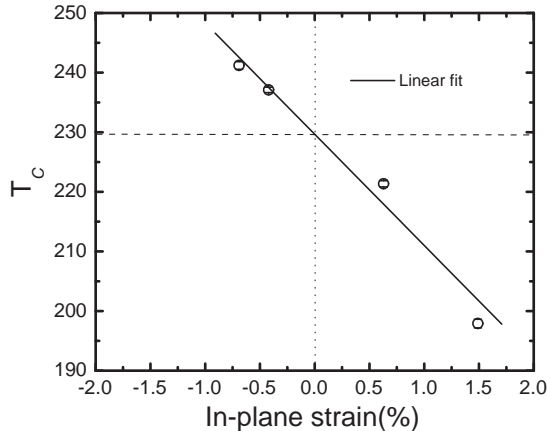


FIG. 3: Phase diagram of Ferromagnetic transition temperature as a function of in-plane strain for films of thickness 22nm. The interpolation to zero strain indicates a  $T_C$  of about 229 K, indicated as the horizontal dashed line.

SLAO(0.3756 nm), LSAT(0.3868 nm) and STO(0.3905 nm). Films on LAO and SLAO are compressed while those on LSAT and STO are under tension. The phase diagram of the ferromagnetic transition temperature  $T_C$  with in-plane strain for these thin films is shown in Fig. 3. The Curie temperature appears to be linearly dependent on the in-plane strain. The interpolation of this plot to the point with zero strain provides an estimate of the reduction of the Curie temperature by finite size scaling alone for a thickness of 22 nm.

We find that the Curie temperature for a film without strain at a thickness of 22 nm would be about 229 K. This allows us to construct a quantitative prediction of  $T_C$  versus thickness due to finite size scaling. According to the theory,[3] the critical shift component is expected to be  $\lambda=1$  for the mean field approximation, which is a reasonable description for an itinerant or double-exchange based ferromagnet. [16] Similarly, de Andres [12] has reported that for manganite films the reduction of  $T_C$  is well fit with  $\lambda=1$ . Thus taking  $\lambda=1$  and  $T_C(\infty) \approx 250$  K, [17] the bulk limit of LSCO, leaves a single fitting parameter,  $c$ , for the finite size effect equation(1). We fit  $c$  in the equation to make  $T_C$  at 22 nm thickness equal to 229 K. This gives a value for  $c$  of 1.848 nm, which corresponds to a spin-spin correlation length of about 9 lattice constants according to a model by Zhang et al., similar to Gd films.[3] The resulting curve is shown as a dashed line in in Fig. 2. Deviation of the actual Curie Temperature from this line for a specific film should be primarily due to the effects of strain on fundamental material parameters.

An examination of Fig. 2 and Fig. 3, along with the discussion above, suggests that in-plane tension sup-

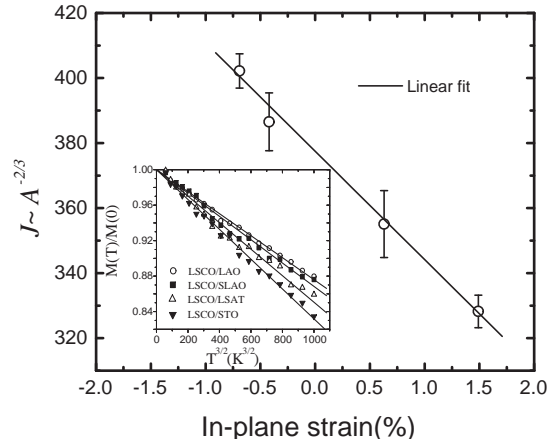


FIG. 4: Exchange interaction  $J(\sim A^{-2/3})$  vs. in-plane strain. The inset shows the reduced magnetization  $M(T)/M(0)$  as a function of  $T^{3/2}$  with an applied magnetic field 100 G for the same films as in Fig. 3. We fit the data according to Bloch's law to derive the spin wave parameter  $A$  and thus  $J$ .

presses the Curie Temperature while in-plane compression enhances it. If this is true, then we expect to see directly a change in the exchange coupling energy,  $J$ , that matches the changes in  $T_C$  seen in Fig. 3. The exchange energy can be derived from Bloch's law. [18, 19] The variation of the spontaneous magnetization  $M(T)$  with the temperature  $T$  at low temperature limit is determined by  $M(T) = M_0(1 - AT^{3/2})$  where  $M_0$  is the spontaneous magnetization at 0 K and  $A$  is a constant, called spin wave parameter. In this model, the exchange interaction  $J$  is proportional to  $A^{-2/3}$ . The reduced magnetization  $M(T)/M(0)$  vs  $T^{3/2}$  in the low temperature region is shown in the inset of Fig. 4. The data are fit to Bloch's law, and the spin wave parameter  $A$  is derived. The exchange interaction, as indicated by  $A^{-2/3}$ , is plotted in Fig.4. There is a strong dependence on in-plane strain, very similar to the linear behavior of the Curie Temperature shown in Fig. 3. According to mean field theory,  $T_C$  is proportional to  $J$  in a bulk magnet. [20] Thus this supports the idea that the primary factor causing the change in  $T_C$  for the films of thickness 22 nm is a change in  $J$  caused by strain. It is precisely these changes in  $J$  that can reveal insights into the origin of magnetism in this compound. A leading theory for the magnetism in LSCO is the double exchange mechanism.[21] This model relies upon Co-O-Co electron hopping so that a strong dependence on bond length is expected. However a proper evaluation of the theory requires an in depth analysis of the local atomic distortions resulting from strain.[22] In a future report on our EXAFS results,[23] we will examine whether the double exchange mechanism quantitatively predicts the strain dependence we have measured.

In summary, the Curie temperature of ferromagnetic  $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$  thin films was studied as a function of film thickness and strain. Both finite-size and strain affect the ferromagnetic properties and  $T_C$ . By studying films with a variety of thickness, grown on a variety of substrates, we were able to quantitatively assign the change in  $T_C$  to the two contributing factors. An analysis

of magnetization data to give the spin interaction energy appears to confirm that this assignment is reasonable. Ferromagnetism is suppressed by tension and enhanced by compression.

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